



Synthesis of glycerol carbonates by transesterification of glycerol in a continuous system using supported hydrotalcites as catalysts

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ABSTRACT

MgAl hydrotalcites have been grown onto α - and γ -Al₂O₃ and characterized by XR diffraction, N₂ and CO₂ adsorption. XRD patterns show the crystallization of hydrotalcites as nanometric crystals. On the calcined supported materials, the thermal desorption of CO₂ evidences the presence of relatively strong basic sites which are absent on the pure supports. The samples supported by α -Al₂O₃ exhibit a higher basic strength than those supported on γ -Al₂O₃. After rehydration, the total number of sites changes only little, but the original sites, presumed to be of Lewis type are converted to stronger Brønsted sites. The synthesis of glycerol carbonate and dicarbonate has been performed by transesterification of glycerol by diethyl carbonate in a green, efficient and selective process catalyzed by these hydrotalcites supported on α - and γ -Al₂O₃. The control of grain size of the support allows to operate in a flow reactor, then to evaluate the extent of deactivation as a function of time on stream at full conversion of glycerol. Stable catalysts are obtained when α -Al₂O₃ is the support.

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1. Introduction

During the last years, a growing interest has been noticed for the development of renewable alternative fuels such as bio-diesel, produced from vegetable oils by transesterification processes with methanol or ethanol. The high bio-diesel production capacity in the European Union and USA could create a surplus of glycerol obtained as by-product in this process. The formation of this glycerol (about 100 g/kg of bio-diesel) [1] represents a considerable technical and economic burden since it is not fully exploited on the market. Therefore, it is especially important to explore new applications for this product as well as alternative strategies for transforming it into new suitable products. A great number of publications have been reported in this field, highlighting the immense activity in the chemistry of glycerol [2]. Several important chemicals can be obtained from glycerol via oxidation, esterification, etherification, acetalisation, dehydrogenation, polymerisation and so on. Glycerol carbonate and its esters are most interesting derivatives of glycerol. They are relatively new materials in the chemical industry and, due to their properties (low toxicity, low flammability and low vapour pressure) have great potential as new component in gas-separation

membranes, non-volatile solvents for dyes, lacquers, pharmaceuticals, detergents, adhesives, cosmetics, and biolubricants [3], and for the synthesis of new functionalized polymers such as polyglycerol [4]. Fuels also represent large scale applications, and Notari and Rivetti [5] recently reported that a mixture containing alkyl esters or fatty acids (bio-diesel) and one or more esters of fatty acids of glycerol carbonate (constituting between 10 and 40 percent of the weight) can be used as fuel.

Traditionally, glycerol carbonate has been synthesized by reaction between glycerol and phosgene [6], but due to the high toxicity of phosgene, alternative routes based on transesterification in basic media of dialkyl or alkylene carbonates have been explored. The current industrial synthesis of glycerol carbonate entails two steps [7]: first ethylene oxide reacts with carbon dioxide to yield the cyclic ethylene carbonate which is further reacted with glycerol to give glycerol carbonate and ethylene glycol. This process involves the use of homogeneous basic catalysts such as sodium bicarbonate or sodium hydroxide introducing some drawbacks such as the neutralization of the base as well as the recovery of the product by distillation under reduced pressure.

The improvement of the economic and environmental feasibility of the industrial synthesis of glycerol carbonate (i.e. reducing the number of steps and waste) entails the design of an optimized direct method for its production. Few references have been found in the literature concerning the production of glycerol carbonate

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using simplified methodologies. Vieville et al. [8] obtained glycerol carbonate (up to 32% after 1 h) by direct carbonation of glycerol in supercritical carbon dioxide in the presence of zeolites and ion exchange resins, using ethylene carbonate as co-reactant. Aresta et al. have recently reported the direct carboxylation of glycerol with carbon dioxide using tin complexes ($n\text{-Bu}_2\text{Sn}(\text{OCH}_3)_2$, $n\text{-Bu}_2\text{SnO}$ and $\text{Sn}(\text{OMe})_2$) as catalysts [9]. However, the best glycerol conversion achieved after 15 h of reaction was below 7%. Catalysts based on zinc, $\text{Zn}(\text{CH}_3\text{C}_6\text{H}_4\text{-SO}_3)_2$, were used by Yoo and Mouloungui [10] to synthesize glycerol carbonate from glycerol and urea. In this case, the conversion achieved was 85% after 1 h of reaction.

The non-toxicity, biodegradability and cleaner production process of alkyl carbonates such as dimethyl or diethyl carbonate (DMC or DEC, respectively) make them green reagents that prevent pollution at the source during synthesis [11]. Moreover, DEC including ethoxy and carbonyl groups can be used as an effective carbonylating and ethylating agent as well as a raw material for manufacturing polycarbonates [12]. Glycerol carbonate can be obtained via a transesterification reaction of DMC with glycerol using homogeneous catalysts such as $n\text{-Bu}_2\text{Sn}(\text{OCH}_3)_2$, resulting in a 65% conversion after 15 h [9]. The usual synthesis is performed using as catalyst large quantities of K_2CO_3 to produce either glycerol carbonate, glycerol dicarbonate or diglycerol tricarbonate depending on the reaction temperature and/or the amount of DMC added [4]. Mouloungui et al. [13] reported the synthesis of glycerol carbonate by reaction of glycerol on a cyclic organic carbonate in the presence of a solid catalyst consisting of an anionic, bi-carbonated or hydroxylated macroporous resin, or alkaline X- or Y-type zeolite. This reaction produces glycol as by product with a selectivity of about 15–30%.

We have recently reported the results of an exploratory study focussed on the synthesis of glycerol carbonate by the transesterification of glycerol with diethyl carbonate using heterogeneous catalysts based on hydrotalcite-like compounds [14]. The results showed that Mg/Al mixed oxides and the rehydrated hydrotalcites are efficient and reusable catalysts for the transesterification reaction, being able to replace homogeneous catalysts, such as K_2CO_3 , which showed similar activity. Along the same research lines, Takagaki et al. showed that an uncalcined hydrotalcite containing a hydromagnesite phase efficiently catalyzes glycerol carbonate synthesis from glycerol and DEC using DMF as solvent [15]. Climent et al. also recently reported that solids with well balanced acid-base pairs such as Zn/Al mixed oxides from hydrotalcite-like compounds are efficient catalysts for the transesterification of glycerol with ethylene carbonate or carbonylation of glycerol with urea [16].

Hydrotalcite-like compounds (HTs) are anionic clays with the general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+} \text{A}^{n-}_{x/n} n\text{H}_2\text{O}$, where M^{II} and M^{III} stand for a divalent and a trivalent cation, respectively, A is a charge-balancing anion and x the value of the stoichiometric coefficient ($x = \text{M}^{\text{II}}/\text{M}^{\text{II}} + \text{M}^{\text{III}}$). HTs are usually prepared by co-precipitation from metal salts in alkaline media at constant pH followed by a hydrothermal treatment of the precipitate. The usual protocol of activation for these materials is controlled thermal decomposition which leads to the formation of mixed oxides showing a good dispersion of metals, a large specific surface area and Lewis basic properties. The rehydration of calcined hydrotalcites under a CO_2 free atmosphere allows the layered structure to be recovered containing interlayer OH^- anions, which provides significant Brønsted basic properties [17,18].

Roelofs et al. [19] proposed that the active sites participating in catalysis are located at the edge of the platelets. Thus, the number of accessible edge active sites is limited by the lateral size of the HT crystallites and increases with decreasing particle size. Consequently, several studies have been conducted to maximize the number of active sites by minimizing the lateral size of the HTs. [20,21] This was achieved by using ultrasound during

reconstruction [20,22] or by preparing small HT platelets ($\approx 20\text{ nm}$) on carbon nanofibers [23]. The resulting catalysts showed a significant increase in catalytic activity in reactions such as self-condensation of acetone and in the condensation of citral with acetone. For practical applications, HTs have the inconvenience to be obtained in very small particle sizes, which can be used in batch reactors but not in continuous flow reactors due to the severe pressure drop.

In this work, particles of α - and γ - Al_2O_3 were used as supports for the synthesis of Mg/Al hydrotalcites by impregnation of Mg and Al precursor salts. After calcination and rehydration, catalysts consisting of HT dispersed on Al_2O_3 with Brønsted basic sites were obtained. The structure of these catalysts is reported. An exploratory study of their catalytic properties for the synthesis of glycerol carbonate has been performed in order to prove the possibility of using these catalysts in a continuous system.

2. Experimental

2.1. Materials

Particles of 0.2–0.3 mm of α - Al_2O_3 ($10\text{ m}^2/\text{g}$) and γ - Al_2O_3 ($115\text{ m}^2/\text{g}$) both from Norton were used as supports. The precursor salts, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity 99%) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purity 98%), were purchased from Sigma–Aldrich.

2.2. Catalysts preparation

In a typical procedure, 4 g of α - or γ - Al_2O_3 were impregnated with 4 mL of a solution containing the appropriate amount of magnesium and aluminum salts (1.6 mmol/g or 2.04 mmol/g of $\text{Mg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and 0.8 mmol/g or 0.5 mmol/g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in deionised water. The impregnated alumina was dried in an oven at 373 K for 1 h and then calcined in a tubular quartz packed bed reactor at 723 K (heating rate: 10 K/min) flowing 30 mL/min of air. At this stage a solid referred as HT α -alpha or gamma is obtained. The rehydration of the supported mixed oxides obtained after this treatment was performed in a closed 100 mL autoclave batch reactor at 473 K for 12 h (containing 5 g of solid and 40 g of decarbonated water) and gives samples referred as HT α -alpha or gamma, where x denotes the Mg/Al molar ratio in solution (2 or 4).

2.3. Analysis and characterization

Specific surface areas of the samples were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2000 equipment. Samples were previously degassed in situ at 393 K under vacuum for 5 h. Surface areas were calculated using the Brunauer–Emmet–Teller (BET) methods over a p/p_0 range where a linear relationship was maintained. X-ray diffraction (XRD) powder patterns were collected on a Siemens EM-10110BU diffractometer model D5000 fitted with a $\text{Cu K}\alpha$ (1.541 Å) radiation source. Data were recorded over a 2θ range of 5–70° with an angular step of 0.05° at 3 s/step which resulted in a scan rate of 1°/min. Patterns were identified using files from the Joint Committee on Powder Diffraction Standards (JCPDS).

The basicity measurements were obtained by temperature programmed desorption (TPD) of CO_2 on a Thermo Finnigan TPDRO 1100 equipped with a TCD detector. Typically, ca. 0.350 g of sample were placed in a tubular quartz reactor. The sample was pretreated with Ar at 353 K during 1 h and then cooled to room temperature and treated with a CO_2 flow (2.5% CO_2 in He). The desorption of CO_2 was measured by heating the sample from room temperature to 1073 K at a heating rate of 10 K/min in He flow, and water was trapped on magnesium perchlorate, in order to avoid interferences. The number of basic sites was calculated from the CO_2

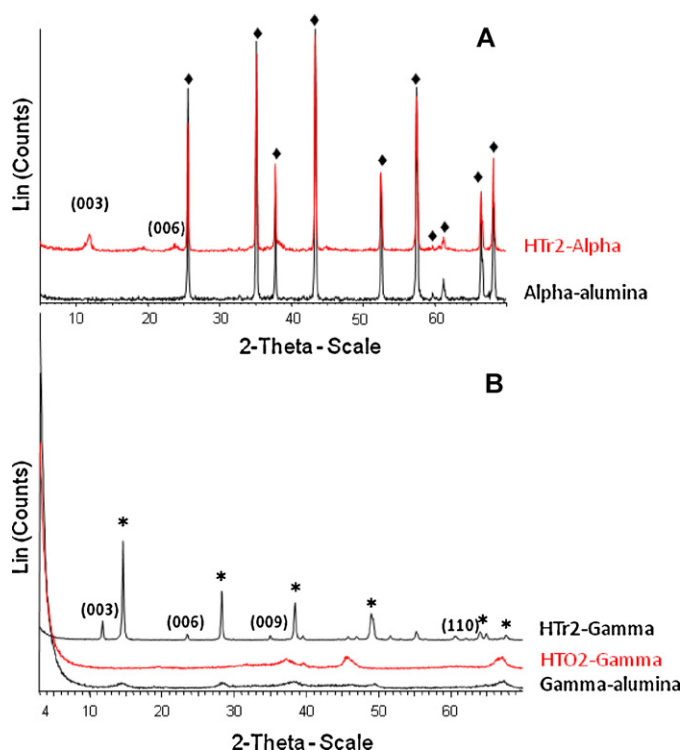


Fig. 1. PXRD diffractograms of: (A) Alpha-alumina supported catalysts and (B) Gamma-alumina supported catalysts. (♦) Corundum phase; (*) Boehmite phase (γ -AlO(OH)).

peaks by deconvolution using the software of the equipment, and a calibration of the instrument using a known amount of CaCO_3 .

2.4. Catalytic activity tests

Glycerol (99%), diethyl carbonate (DEC) (99.5%, GC grade) and dimethyl sulphoxide (DMSO) as solvent (99%) were purchased from Aldrich and used without any further purification. Transesterification reaction was performed in a continuous system formed of a tubular quartz packed bed reactor, a furnace equipped with a temperature controller, a Gilson pump and an inlet for flowing 3 mL/min of Ar. The mixture of reactants, containing glycerol (1.85 g), DEC (38.95 g) and solvent (21.90 g) was fed into the preheated reactor containing 4 g of fresh catalyst with a feed flow of 0.1, 0.05 or 0.025 mL/min.

The influence of the support, the type of solvent used as well as the amount of magnesium added and the activation form of catalysts were studied.

Samples were periodically collected and quantified by GC analysis equipped with a FID detector. This was performed on a Shimadzu GC-2010 with a Zebtron ZW-WAX capillary column.

3. Results and discussion

3.1. Catalyst characterization

PXRD patterns of alpha and gamma-supported samples are displayed on Fig. 1A and 1B. The patterns of the samples supported on α -Al₂O₃ (Fig. 1A) show the peaks characteristic for corundum phase (JCPDS: 042-1468). Additional peaks were observed on rehydrated sample corresponding to (003) and (006) reflection planes of meixnerite phase (JCPDS: 22-700) obtained after rehydration of magnesium and aluminum mixed oxides. In addition, the sample HTr2-alpha developed new diffraction peaks identified as boehmite

phase (JCPDS: 01-088-2112), attributed to the rehydration of part of the alumina which has not reacted to form hydrotalcite. Diffraction lines of boehmite (γ -AlO(OH)) and meixnerite were also clearly detected on rehydrated samples supported by γ -Al₂O₃ (Fig. 1B) indicating that at least part of the γ -Al₂O₃ support was transformed into boehmite after the rehydration treatment. This sample also exhibits at $d = 1.52$ nm the (110) reflexion of HT, which can be used to determine the a lattice parameter of HT on the support. The Al/Mg + Al ratio obtained from the Vegard's law is close to 0.3, as expected from the composition used in the synthesis. (Table 1) On the other hand, the catalyst prepared with higher amount of magnesium (HTr4-Alpha) presented a (110) reflexion at $d = 1.527$ nm revealing the formation of a hydrotalcite with an Al/Mg + Al of approximately 0.3 instead of 0.2, as expected from the Mg/Al molar ratio in the solution. From this result, we can suppose that catalyst HTr4-Alpha contains an extra-phase of MgO(H) not detected by PXRD.

The transformation of γ -Al₂O₃ into a hydrated phase has already been described by other authors [24,25] and can occur even at room temperature [26]. The hydrated species formed depend on variables such as pH of the media, temperature, pressure and others. The size of the particles of HT was computed from the Scherrer equation using the (003) line width. The results reported in Table 1, show the formation of particles in the nanometric range, with a smaller size when α -Al₂O₃ is the support. The average size obtained about 13.5 nm is comparable to that reported for HT on C nanofibers [21].

The restructuring of the solid by hydration–dehydration may also involve physico-chemical changes in the support relative to the pore structure and surface acid–basic properties, [25,27] that can affect the catalytic properties such as activity, selectivity or stability during time on stream. The specific surface area and textural parameters of the supports and catalysts are reported in Table 1. As was seen in PXRD analysis, the hydrothermal treatment of the catalyst produced structural changes in the support, making the material more crystalline and increasing the crystallite size; consequently a notable decrease in specific surface area, more marked in catalysts supported on γ -Al₂O₃, is observed. The final solid shows an average pore size of about 6–7 nm, in the range of mesopores.

The basicity of the support, supported mixed oxides and hydrothermally treated catalysts was measured by TPD-CO₂ and the basic strength could be assigned according to the temperature at which peaks appeared (Fig. 2). The number of basic sites was estimated by deconvolution and integration of these peaks (Table 2).

Both alpha and gamma supported catalysts showed similar TPD-CO₂ profiles. Hydrated catalysts presented an intense peak around 775 K which can be assigned to the decomposition of bicarbonate species, formed by adsorption of CO₂ on the Brønsted basic sites of the rehydrated hydrotalcites [21]. Calcined catalyst supported on alpha alumina also presented a weak desorption at this temperature, indicating a lower amount of Brønsted basic sites on the surface of mixed oxides. A second peak around 900 K is observed on both the calcined and hydrated samples and could be ascribed to strong Lewis basic sites, i.e. O²⁻ linked to coordinatively unsaturated Mg species (corner or edges).

Gamma supported samples presented low temperature peaks between 443 K and 458 K, more intense on the calcined sample, which can be assigned to an adsorption on Lewis sites identified to oxygens linked to Al cations, since pure γ -Al₂O₃ presented the same desorption peak. When γ -Al₂O₃ is used as support, the desorption peaks are shifted towards lower temperatures compared to those observed for HT/ α -Al₂O₃. This change in basic strength is more marked on calcined samples, suggesting a high interaction of mixed oxides on the γ -Al₂O₃ support. The temperature corresponding to the desorption of CO₂ observed on these supported HT

Table 1

BET specific surface area, textural properties and XRD characterization of catalysts and supports.

Catalyst	BET surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Average pore diameter ^b (nm)	XRD analysis		
				Phase ^c	HT crystallite size ^d (nm)	HT phase composition (Al/Mg + Al) ^e
α-Al ₂ O ₃	14	–	–	Corundum	–	–
HTO2-Alpha	15	–	–	Periclase + corundum	–	–
HTO4-Alpha	15	–	–	Periclase + corundum	–	–
HTr2-Alpha	17	–	–	Meixnerite + boehmite + corundum	13.5	0.3
HTr4-Alpha	23	–	–	Meixnerite + corundum	14.9	0.3
γ-Al ₂ O ₃	246	0.47	7.59	–	–	–
HTO2-Gamma	226	0.37	6.57	Periclase	–	–
HTO4-Gamma	200	0.35	6.93	Periclase	–	–
HTr2-Gamma	64	0.25	15.91	Meixnerite + boehmite	21.8	0.3
HTr4-Gamma	139	0.29	8.17	Meixnerite + boehmite	20.2	–

^a Determined from the nitrogen adsorbed volume at $p/p_0 = 0.984$.^b Determined from the maximum of BJH pore size distribution.^c Observed by XRD analysis.^d Calculated with Scherrer equation using LaB₆ as patron.^e Calculated from (1 1 0) reflexion by using the Vegard's law.

is higher than that reported for bulk HT: in that case the peak of CO₂ was observed at 600–700 K [28,29], compared to >700 K here. This effect is due in part to the higher rate of increase of temperature in the TPD (10 K/min here compared to 5 K/min) which shifts the peaks up to 723 K, as reported by Sanchez Valente et al. [30]

Table 2 shows that the strong basicity is introduced onto alumina by the addition of HT, and that a rather similar number of basic sites is measured for either calcined or rehydrated catalysts. On bulk samples, the determination of basicities using calorimetric adsorption of CO₂ [31] showed a lower number of sites and a lower heat of adsorption for rehydrated samples. On smaller particles, the small difference observed here shows that the equilibrium of CO₂ between the bulk and the surface is fast at the temperature of 353 K used for the adsorption, leading to the same amount adsorbed on calcined and rehydrated samples. The main difference is then the higher number of Brønsted basic sites on the rehydrated samples.

3.2. Catalytic activity

An exploratory study of the transesterification of glycerol with DEC was made in order to check whether a continuous flow reactor could be used, with these calcined/hydrated materials as catalysts. The reaction was performed at a constant temperature (403 K) and the mixture of reactants, containing glycerol (1.85 g), DEC (38.95 g) and solvent was fed into the pre-heated reactor (containing 4 g of fresh catalyst). The dependence of parameters such as solvent, feed flow rate, support and hydration of catalysts was studied.

3.2.1. Effect of the solvent and feed flow rate

The selection of the solvent is an important aspect to consider in the design of an experiment. The main function of the solvent is the solubilization of the reactants and the products. However, the presence of a solvent in the media can modify aspects of the reaction such as yield and selectivity. Since the reactants are strongly polar (glycerol) and aprotic (dimethyl carbonate), three different aprotic polar solvents: dimethyl sulphoxide (DMSO), dimethyl formamide (DMF) and dimethyl acetamide (DMA), were tested in the continuous reaction in order to find the best solution.

Fig. 3 reports the glycerol conversion for the different solvents. A significant effect of the solvent was observed, with the highest conversion close to 50% found for dimethyl sulphoxide (DMSO), falling to 30% or 20% for dimethyl formamide (DMF) or dimethyl acetamide (DMA), respectively.

The properties of these solvents are displayed on Table 3. The glycerol conversion is correlated to the polarity of the solvent, and increases with an increase in polarity measured by the dipolar moment or dielectric constant values. This is in accordance with literature reports [32,33] in which a higher catalytic activity for hydrotalcite-like compounds with solvents with higher polarity has been observed. This could be due to a better desorption of the products from the hydrophilic surface of the catalyst.

Three different flow rates were tested (Fig. 4) using DMSO as solvent. The conversion increases proportionally with the contact time up to 20 min^{−1} (flow 0.05 mL/min), and total conversion is reached at the lower flow. This result proves that the rate is not controlled by extra-particle mass transfer. The rate computed from these results

Table 2

Results of basic properties for the samples.

Sample	TPD analysis of adsorbed CO ₂				Total evolved CO ₂ (μmol g ⁻¹)
	Desorption peaks				
	<500 K	500–600 K	650–850 K	>850 K	
α-Al ₂ O ₃	5 (436) ^a	–	–	–	5
HTO2-Alpha	–	39 (585)	19 (756)	–	58
HTO4-Alpha	–	33 (579)	27 (743)	–	60
HTr2-Alpha	–	–	62 (776)	17 (882)	79
HTr4-Alpha	–	–	59 (749)	9 (880)	68
γ-Al ₂ O ₃	35 (443)	–	–	–	35
HTO2-Gamma	53 (457)	50 (513)	–	19 (880)	122
HTr2-Gamma	9 (458)	–	128 (729)	9 (898)	146

^a Temperature of maximum (K).

Table 3
Properties of the tested solvents.

Solvent	pKa	Polarity	Boiling point (K)	Dielectric constant	Dipole moment	Glycerol conversion (%)
DMSO	35	7.2	462	46.68	4.1	50
DMF	–	6.4	426	36.71	3.86	30
DMA	–	6.5	439	37.78	3.72	20

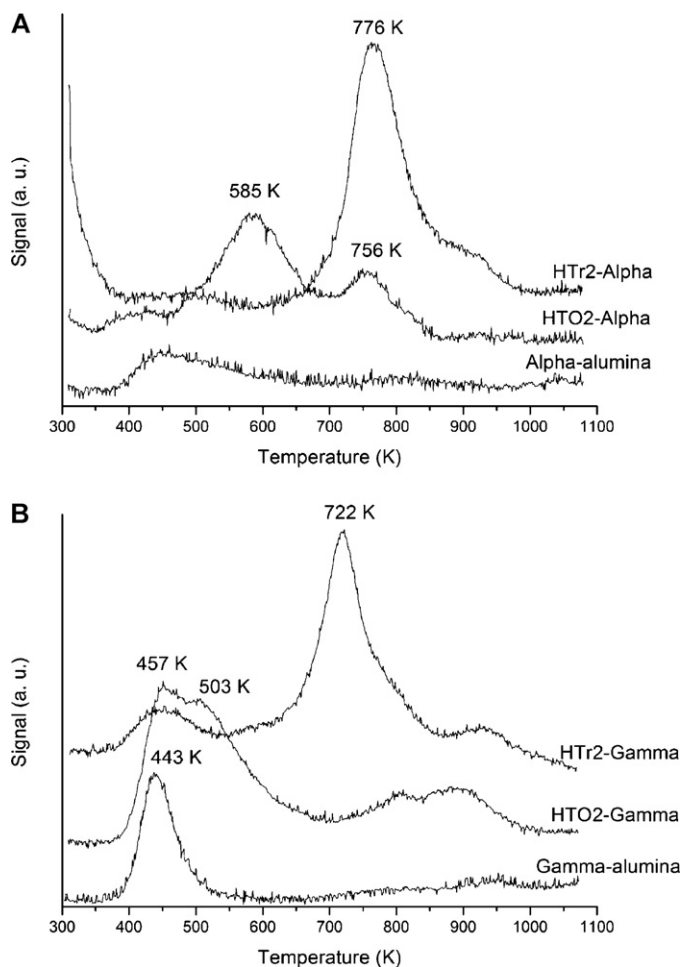


Fig. 2. TPD-CO₂ profiles of: (A) catalysts supported onto alpha-alumina and (B) catalysts supported onto gamma-alumina.

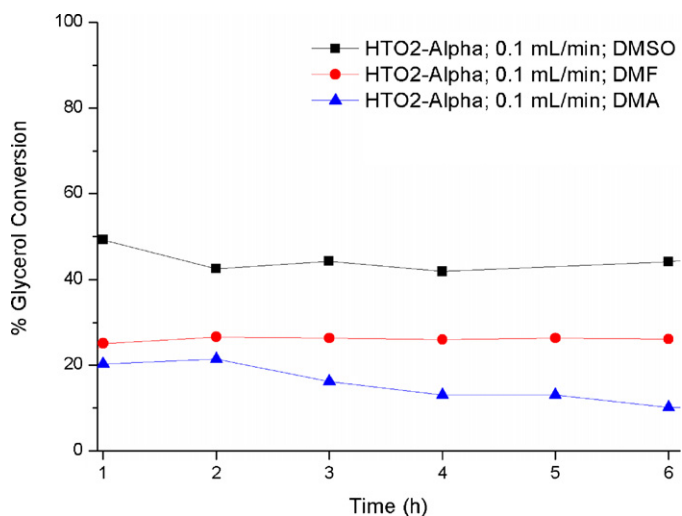


Fig. 3. Glycerol conversion found for catalyst HTO2-Alpha for the three different solvents tested at 403 K and a fixed feed flow of 0.1 mL/min.

is $5 \times 10^{-8} \text{ mol s}^{-1} \text{ g}^{-1}$. The possibility of diffusional limitations can be estimated computing the Thiele modulus modified by Weisz [34].

$$\varphi = \frac{\nu R^2}{(D_{\text{eff}} C_0)}$$

where ν is the rate ($\text{mol s}^{-1} \text{ g}^{-1}$), R the radius of the catalyst grains (here 0.01 cm), C_0 the concentration of glycerol ($3 \times 10^{-4} \text{ mol ml}^{-1}$), and D_{eff} the diffusion coefficient (taken as $10^{-4} \text{ cm}^2 \text{ s}^{-1}$) is about 0.02. Diffusion limits the overall process when $\varphi = 1$, therefore intraparticle diffusion does not limit the process. The variation of selectivities as a function of conversion (insert of Fig. 4) shows that DGC is formed from GC in a consecutive reaction.

3.2.2. Effect of the support and hydration of catalysts

Catalysts were activated by calcination (called HTO2-Alpha or HTO2-Gamma) or by hydration of the calcined catalysts (called HTr2-Alpha or HTr2-Gamma). The following conditions were used for all the catalysts: a feed flow of 0.05 mL/min, a temperature of 403 K and DMSO as solvent. The pure supports, $\alpha\text{-Al}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$, presented no catalytic activity at all.

Fig. 5 shows the catalytic behavior for calcined catalysts. Two different products, glycerol carbonate (GC) and glycerol dicarbonate (GDC), were obtained under these reaction conditions (Scheme 1). The primary alcohols are presumably more reactive than the secondary alcohol, however, once the transesterification of the primary alcohol occurs, the intramolecular reaction between the secondary alcohol and the nearby carbonate group is favored, thus producing GC. Finally, the transesterification reaction between GC and the DEC leads to the formation of GDC.

A possible reaction mechanism is proposed in Scheme 2. First, glycerol is coordinated as a bidentate ligand to the catalyst surface by hydrogen bonds activating the oxygen atoms as nucleophiles. This bidentate coordination is proposed due to the absence of mono-transesterification products. The oxygen of the primary alcohol attacks the carbonylic carbon atom of diethyl carbonate producing the liberation of an ethanol molecule. Then, the oxygen atom of the secondary hydroxyl group attacks the carbonylic carbon atom again in an intramolecular transesterification, which is favored due to the stable geometry of the five member cycle formed. A second molecule of ethanol is generated and glycerol carbonate is desorbed from the surface of the catalyst. When the concentration of glycerol carbonate is high enough, it is coordinated to the surface of the catalyst by its free hydroxyl group which acts as a nucleophile producing a new transesterification leading to the formation of glycerol dicarbonate and a new molecule of ethanol.

For calcined catalysts, the results of Fig. 5 show that the catalytic activity of the samples supported on alpha alumina is higher than that of the samples supported on gamma alumina. Catalyst HTO2-Alpha reached 78% conversion of glycerol, constant as a function of time, whereas HTO2-Gamma achieved only a 20% of conversion. This result is in line with the lower strength of basic centers showed by the calcined sample supported on gamma-alumina, as revealed by the TPD-CO₂ analysis. The higher selectivity of HTO2-Alpha to GDC can be accounted for by the higher conversion.

The catalytic activity was improved when the catalysts were rehydrated (Fig. 6). Both supported alpha and gamma alumina

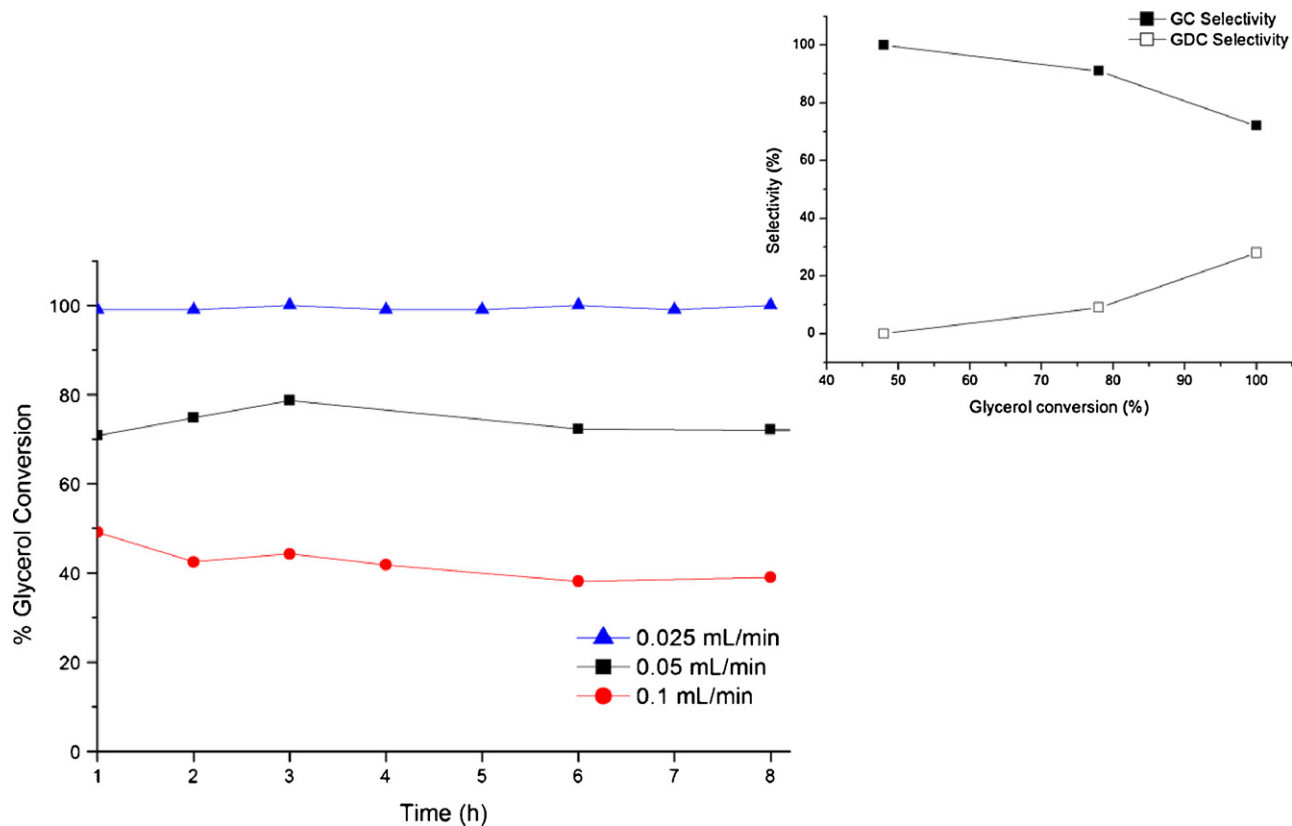
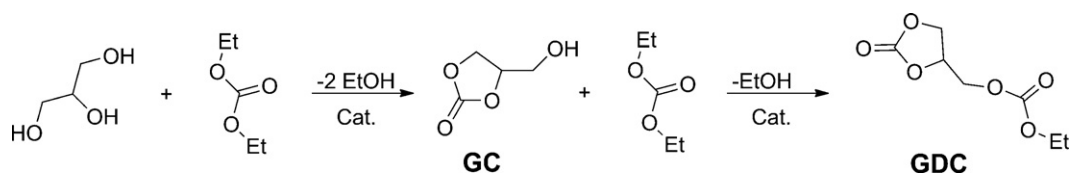
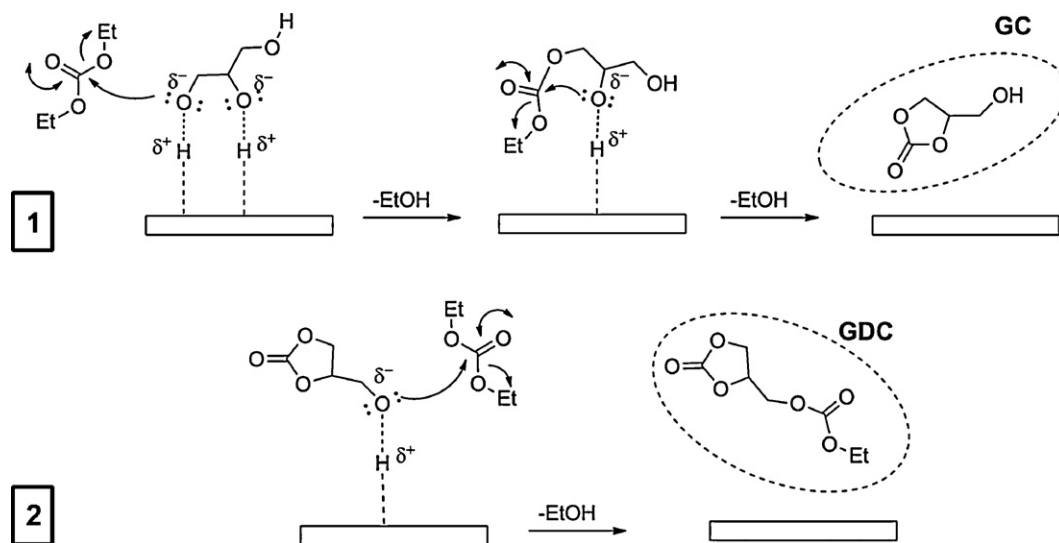


Fig. 4. Results of the variation in HTO2-Alpha catalyst performance for the transesterification of glycerol with diethyl carbonate at 403 K by varying the feed flows. Insert: variation of the selectivity to glycerol dicarbonate with the conversion.



Scheme 1. Consecutive hydrotalcite-catalyzed transesterification reaction of glycerol with DEC.



Scheme 2. Proposal of mechanism of hydrotalcite-catalyzed transesterification of glycerol with DEC.

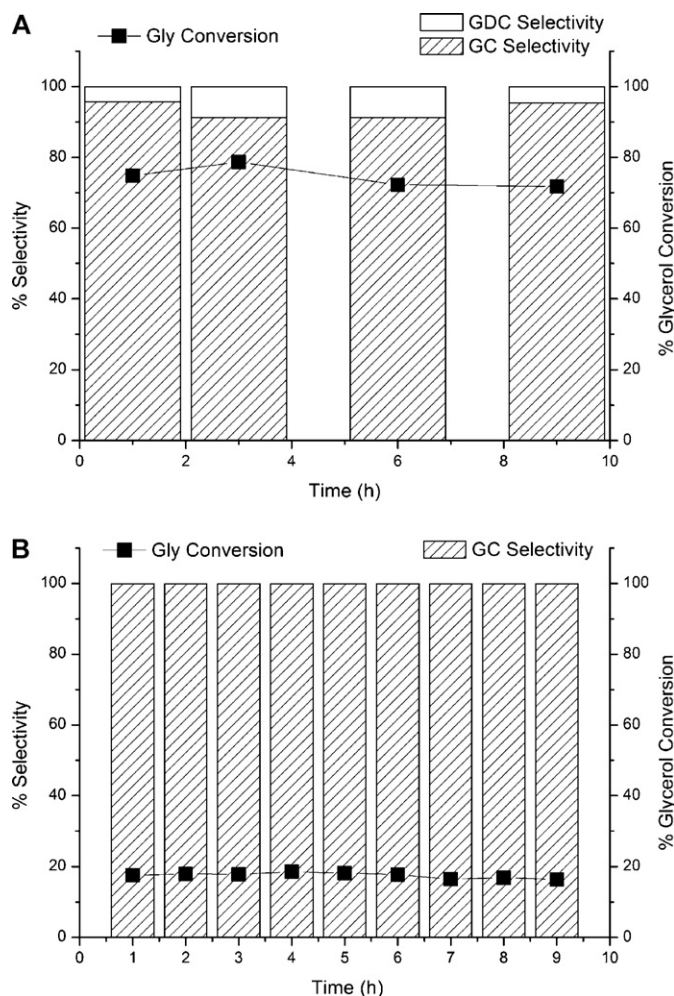


Fig. 5. Catalytic behavior (conversion and selectivity) of calcined catalysts at 403 K and a feed flow of 0.05 mL/min. (A) HTO2-Alpha and (B) HTO2-Gamma.

catalysts then reach total glycerol conversion. If we take into account the similar number of basic sites between calcined and hydrated samples (Table 2) onto a same support and the differences in surface area for catalysts supported on gamma and alpha alumina, the rehydrated catalysts show definitively better catalytic properties than the calcined ones. This suggests that the presence of Brönsted basic sites is an important factor that induces a better catalytic performance in the transesterification of glycerol, as has been observed in literature [14,35].

At a comparable conversion of about 90%, both rehydrated catalysts, HTr2-Alpha and HTr2-Gamma, led to the formation of GC and GDC, but the maximum amount of GDC achieved by HTr2-Gamma catalyst (2.6%) was rather low compared to that obtained on HTr2-Alpha (40.8%). The selectivity to GDC decreased with time of stream on both catalysts: HTr2-Alpha yielded about 40% of GDC in the first hours of reaction dropping to 23.6% of GDC after 8 h, while HTr2-Gamma yielded only 2.6% of GDC in the first hours of stream, decreasing rapidly to obtain pure GC. This deactivation is more marked on HTr2-Gamma and affects only the glycerol conversion, while the sample HTr2-Alpha maintained a total conversion during all the experiment, with a selectivity to GC close to 70%. The consecutive scheme of this reaction is formally analog to a rake scheme [36,37]: in this scheme, at a given conversion level, the selectivity to GDC is determined by the ratio rate of reaction/rate of desorption of GC. The rate of desorption of GC is controlled by the basicity of the surface, and therefore the selectivity to GDC should

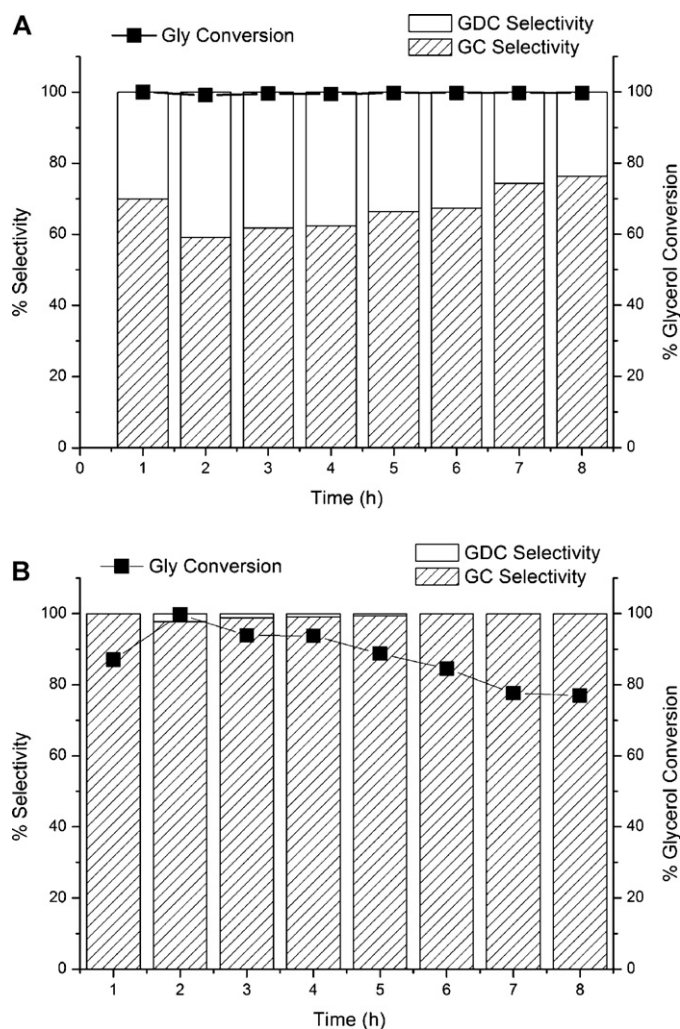


Fig. 6. Catalytic activity for rehydrated catalysts at 403 K and a feed flow of 0.05 mL/min. (A) HTr2-Alpha and (B) HTr2-Gamma.

be higher when the basic strength increases. This effect accounts for the higher selectivity of HTr2-Alpha for GDC, in agreement with the results of TPD.

Catalysts supported on gamma-alumina (HTr2-Gamma and HTO2-Gamma) showed lower conversions than catalysts supported on alpha-alumina despite their higher surface area. The BET surface area of the pure γ - Al_2O_3 was 246 m^2/g and the pore volume and pore diameter were 0.47 cm^3/g and 7.59 nm, respectively. After impregnation of nitrates, BET surface area and pore volume of rehydrated catalysts decreased remarkably (Table 1), however the average pore diameter increased. This behavior is more marked in catalyst HTr2-Gamma than HTr4-Gamma. Thus, the effect of the support is clearly evident on catalytic activity, being the catalysts supported on α - Al_2O_3 more active and stable.

Deactivation can be provoked for instance by the hydrolysis of diethylcarbonate producing an acid moiety which would block the basic sites. This reaction involving water is expected to be facilitated on hydrated catalysts. The fact that the catalyst supported by α -alumina are more stable than those supported by γ -alumina can be related to their high surface area, with a higher retention of water compared to α -alumina of low surface area.

3.2.3. Effect of the amount of magnesium

It is well known that the ratio Mg/Al is an important factor in the catalytic activity of HTs. Indeed other authors have reported an

Table 4

Catalytic behavior of catalysts with different Mg/Al molar ratio.

Catalyst	Mg/Al molar ratio ^a	% Glycerol conversion ^b	% GC selectivity ^b	% GDC selectivity ^b
HTO2-Alpha	2	72	95.4	4.6
HTO4-Alpha	4	98.5	79.5	20.5
HTr2-Alpha	2	99.7	76.4	23.6
HTr4-Alpha	4	83.9	100	–
HTO2-Gamma	2	20	100	–
HTr2-Gamma	2	80	100	–

^a Nominal value.^b After 8 h of continuous stream.

increase of the activity of HT for transesterification reactions when the Mg content increased [38,39].

In order to check the influence of the amount of magnesium contained in catalysts in the catalytic activity, two new catalysts were synthesized by impregnation of particles of α -Al₂O₃ with a magnesium and aluminum nitrate solution with a Mg/Al molar ratio of 4 instead of 2. As reported above the Mg/Al ratio in the hydrotalcites phase is indeed practically constant. Catalysts were activated by calcination and rehydration of calcined materials as done in previous catalyst. The amounts of CO₂ adsorbed by these solids are reported in Table 2: they are rather close to those observed with the other preparations.

Fig. 7A shows the catalytic behavior of the calcined catalyst, HTO4-Alpha. The catalyst presented total glycerol conversion

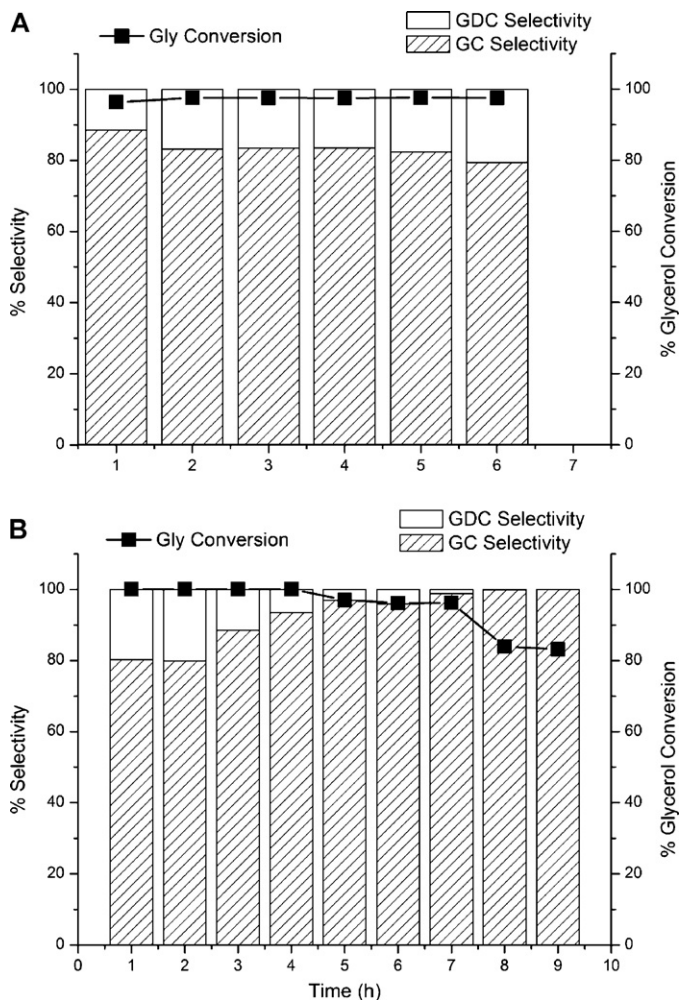


Fig. 7. Catalytic activity for catalysts with higher Mg content: (A) calcined catalyst, HTO4-Alpha and (B) rehydrated catalyst, HTr4-Alpha.

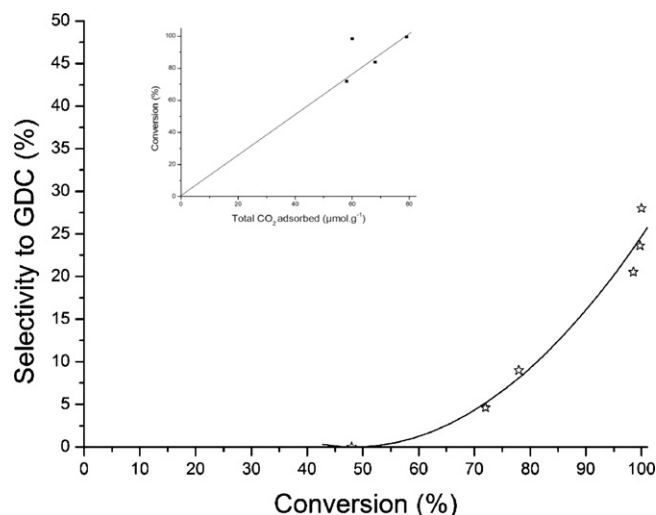


Fig. 8. Selectivities of the catalysts supported on α -alumina as a function of the conversion. Insert: variation of the conversion with the amount of CO₂ adsorbed.

during all the experiment (8 h) and the selectivity to GDC was maintained almost constant (around a 20%). When the catalyst was rehydrated (Fig. 7B), total glycerol conversion was also achieved, but after 8 h on stream a small deactivation occurred manifested by both a loss of glycerol conversion and a loss of the secondary product of transesterification (GDC). The glycerol conversion dropped to 88% after 9 h and the selectivity towards GDC initially 20% dropped and the reaction became completely selective to the product of the primary product of transesterification, GC.

Table 4 reports the different catalytic behaviors of the catalysts with higher content in magnesium compared to the previous ones. Calcined catalysts showed a higher glycerol conversion and a higher selectivity to glycerol dicarbonate at the expenses of glycerol carbonate, with increasing magnesium content. All the points of this Table 4 are reported on a graph selectivity versus conversion (Fig. 8), and fit the same curve, showing that the selectivity to GC is determined by the conversion. On the other hand, the conversion is roughly proportional to the amount of CO₂ adsorbed (insert in Fig. 8). 90% selectivity to glycerol carbonate can be reached at about 80% conversion using these catalysts showing a good stability as a function of time.

4. Conclusions

In conclusion, we have developed an efficient method for the obtention of hydrotalcites supported on α -Al₂O₃ or γ -Al₂O₃. These solids can be activated like bulk HT by calcinations and further rehydration. Due to their better mechanical properties, these solids can be used in a continuous flow reactor. They are active for the conversion of glycerol into glycerol carbonate and glycerol dicarbonate.

Due to the immiscibility of glycerol and diethyl carbonate, the reaction was carried out using a solvent to favor the flow of

reactants through the catalytic system. Different polar solvents were evaluated in the glycerol transesterification, among which dimethyl sulphoxide (DMSO) is the most favorable.

The experimental results show that the type of basic centre has a significant influence on the activity in the transesterification reaction. Thus, catalysts which present Brønsted basicity (rehydrated catalysts) showed better performances than calcined samples which present mainly Lewis basic sites. In addition, the stronger adsorption at the Brønsted sites favors the consecutive transesterification of the glycerol carbonate. Moreover, it has been observed that the most active catalysts lead to a higher yield of GDC produced at the expenses of glycerol carbonate.

An increase in the magnesium content in the catalyst led to a higher glycerol conversion and higher yield of GDC, however catalyst HTr4-Alpha showed lower stability than catalyst HTr2-Alpha, probably due to the presence of an extra-phase of MgO(H) in the catalyst.

On the other hand, the support effect on catalytic properties is clearly evident, the catalysts supported on α -Al₂O₃ being more active. This higher activity is accounted for by the stronger basicity of hydrotalcites supported onto α -Al₂O₃ due to the weak interaction between the hydrotalcite and the support, evidenced by TPD of CO₂.

Thus, it is concluded that hydrotalcite-type compounds are promising candidates for the continuous transesterification reaction, being possible substitutes of homogeneous catalysts used for this propose and opening the possibility of processes in continuous reactors.

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References

[1] D. Fabbri, V. Benovi, M. Notari, F. Rivetti, *Fuel* 86 (2007) 690.

- [2] Y. Zheng, X. Chen, Y. Shen, *Chem. Rev.* 108 (2008) 5253.
- [3] D. Herauld, A. Eggers, A. Strube, J. Reinhard, DE101108855A1 (2002).
- [4] G. Rokicki, P. Rakoczy, P. Parzuchowski, M. Sobiecki, *Green Chem.* 7 (2005) 529.
- [5] M. Notari, F. Rivetti, to Polimeri Europa, US20050261144 (2005).
- [6] A.G. Shaikh, S. Sivarani, *Chem. Rev.* 96 (1996) 951.
- [7] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chem.* 10 (2008) 13.
- [8] C. Vieville, J.W. Yoo, S. Pelet, Z. Mouloungui, *Catal. Lett.* 56 (4) (1999) 245.
- [9] M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, *J. Mol. Catal. A: Chem.* 257 (2006) 149.
- [10] J.W. Yoo, Z. Mouloungui, *Stud. Surf. Sci. Catal.* 146 (2003) 757.
- [11] P. Tundo, M. Selva, *Acc. Chem. Res.* 35 (9) (2002) 706.
- [12] D. Wang, B. Yang, X. Zhai, L. Zhou, *Fuel Process. Technol.* 88 (2007) 807.
- [13] Z. Mouloungui, J.W. Yoo, C.A. Gachen, A. Gaset, G. Vermeersch, EP0739888 (1996).
- [14] M.G. Álvarez, A.M. Segarra, S. Contreras, J.E. Sueiras, F. Medina, F. Figueras, *Chem. Eng. J.* 161 (2010) 340.
- [15] A. Takagaki, K. Iwatani, S. Nishimura, K. Ebitani, *Green Chem.* 12 (2010) 578.
- [16] M.J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepción, *J. Catal.* 269 (2010) 140.
- [17] R. Tessier, D. Tichit, F. Figueras, J. Kervenal, FR2729137 (1995).
- [18] D. Tichit, M. Naciri Bennani, F. Figueras, R. Tessier, J. Kervennal, *Appl. Clay Sci.* 13 (1998) 401.
- [19] J.C.A. Roelofs, A.J. van Dillen, K.P. de Jong, *Catal. Today* 60 (2000) 297.
- [20] S. Abelló, F. Medina, D. Tichit, J. Pérez-Ramírez, Y. Cesteros, P. Salagre, J.E. Sueiras, *Chem. Commun.* (2005) 1453.
- [21] F. Winter, V. Koot, A.J. van Dillen, J.W. Geus, K.P. de Jong, *J. Catal.* 236 (2005) 91.
- [22] M.J. Climent, A. Corma, S. Iborra, K. Epping, A. Velty, *J. Catal.* 225 (2004) 316.
- [23] F. Winter, A.J. van Dillen, K.P. de Jong, *Chem. Commun.* (2005) 3977.
- [24] H. Ly, Y. Xu, C. Gao, Y. Zhao, *Catal. Today*, doi:10.1016/j.cattod.2010.07.015.
- [25] L. Yun-Cheng, X. Lan, X. Feng, W. Zhan-Wen, W. Fei, *Appl. Surf. Sci.* 253 (2006) 766.
- [26] G. Lefèvre, M. Duc, P. Lepeut, R. Caplain, M. Fédoroff, *Langmuir* 18 (2002) 7530.
- [27] X. Yang, Z. Sun, D. Wang, W. Forsling, *J. Colloid Interface Sci.* 308 (2007) 395.
- [28] D. Tichit, M.H. Lhouty, A. Guida, B. Chiche, F. Figueras, A. Auroux, E. Garrone, *J. Catal.* 151 (1995) 50.
- [29] S. Abelló, F. Medina, D. Tichit, J. Pérez-Ramírez, J.C. Groen, J.E. Sueiras, P. Salagre, Y. Cesteros, *Chem. Eur. J.* 11 (2005) 728.
- [30] J. Sanchez Valente, J. Prince, A.M. Maubert, L. Lartundo-Rojas, P. Ángel, G. Ferrat, J.G. Hernández, E. Lopez-Salinas, *J. Phys. Chem. C* 113 (2009) 5547.
- [31] J. Sanchez Valente, F. Figueras, M. Gravelle, P. Kumbhar, J.##J. Lopez, P. Besse, *J. Catal.* 189 (2000) 370.
- [32] D. Tichit, D. Lutić, B. Coq, R. Durand, R. Teissier, *J. Catal.* 219 (2003) 167.
- [33] D. Kishore, S. Kannan, *J. Mol. Catal. A* 223 (2004) 225.
- [34] P.B. Weisz, *Science* 179 (1973) 433.
- [35] A. Corma, S.B.A. Hamid, S. Iborra, A. Velty, *J. Catal.* 234 (2005) 340.
- [36] J.M. Tatibouët, J.E. Germain, C.R. Acad. Sci. Paris 289 (II) (1979) 305.
- [37] M. Cozzolino, R. Tesser, M. Di Serio, P. D'Onofrio, E. Santacesaria, *Catal. Today* 128 (2007) 191.
- [38] D.G. Cantrell, L.G. Gillie, A.F. Lee, K. Wilson, *Appl. Catal. A: Gen.* 287 (2005) 183.
- [39] H. Zeng, Z. Feng, X. Deng, Y. Li, *Fuel* 87 (2008) 3071.